

# CLOSE PACKING OF ATOMS, GEOMETRIC FRUSTRATIONS AND THE FORMATION OF HETEROGENEOUS STATES IN CRYSTALS

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## Abstract

To describe structural peculiarities in inhomogeneous media caused by the tendency to the close packing of atoms a formalism based on the using of the Riemann geometry methods (which were successfully applied lately to the description of structures of quasicrystals and glasses) is developed. Basing on this formalism we find in particular the criterion of stability of precipitates of the Frank-Kasper phases in metallic systems. The nature of the "rhenium effect" in W-Re alloys is discussed.

Recently the interest grows to the significance of crystallogometrical factors, first of all connected with the close packing of atoms, for the structure of condensed matter [1]. There is a whole class of metallic systems which structure is apparently determined by the tendency to the close packing of ionic spheres with different radii including quasicrystals, metallic glasses [1], small metallic clusters [2] and Frank-Kasper (FK) phases [3]. It is worthwhile to stress that the considerations of the closest local packing may contradict with the existence of long-range crystal order. It distinguishes essentially the real three-dimensional case from the two-dimensional one where (for the case of spheres of equal radii) the triangle lattice provides the closest packing both for the whole space and its every part i.e. both globally and

locally [4]. Classical problem about the distribution of spheres in three-dimensional space to obtain the closest packing has not yet solved rigorously (it is the part of the 18th Gilbert problem). However, it is known that spheres may be packed locally with higher density than in fcc, hcp and other close packed lattices [4]. Therefore the situation of geometric frustrations arises when the optimum structure from the point of view of local surrounding cannot be optimum globally. The concept of frustrations appeared to be useful in particular for the consideration of the structure of disordered systems [1,5].

The cause of the existence of the geometric frustrations is the fact that the *Euclidean* space cannot be occupied completely by regular tetrahedra (the regular tetrahedron is the structure unit providing the closest packing of four atom groups). An elegant technique has been proposed in Ref.6 to construct the structures of FK phases when the latter are obtained from the closest packing of tetrahedrons in *Riemannian* space by the introducing of the net of structure disclinations (SD) decurved the space and then the filling of the Euclidean space by the structure units arisen. Here we will use a similar approach to analyze the problem of formation of heterogeneous state (HS) in metallic alloys. Such state is the subject of great interest of researchers in the field of material science lately. From the experimental point of view it is distinguished by the peculiar diffuse X-ray scattering corresponding in the real space to the presence of relatively small clusters containing only hundreds or even tens of atoms [7]. The examples are the so called athermic  $\omega$ -phase in some Ti- and Zr-based alloys [8] and in  $\text{Cr}_{1-x}\text{Al}_x$  [9],  $\sigma$ -phase in  $\text{Fe}_{1-x}\text{Cr}_x$  [10], precipitates of  $\text{W}_3\text{Re}$  phase with A15 structure in  $\text{W}_{1-x}\text{Re}_x$  [11]. Recent investigations of  $\text{Ti}_{1-x}\text{Fe}_x$  alloys by Moessbauer effect [12] have shown the presence of geometric frustrations i.e. the difference of the type of short-range order in local surrounding of Fe nuclei from the long-range order in a crystal as a whole. The hypothesis has been proposed in Ref. 13 about the existence of small icosahedral clusters in this alloys.

Generally speaking, the structure of crystal phases is determined by the whole number of factors. Among them, apart from the considerations of close packing, the spatial orientation of covalent bonds, peculiarities of electronic structure near the Fermi surface etc are the

most frequently discussed. Therefore it is naturally to expect that the nature of HS may be different for different systems. In particular Krivoglaz [7] stressed the role of peculiar features of the shape of the Fermi surface for the formation of HS in Ti- and Zr-based alloys. This mechanism is however hardly to be universal since in the whole number of systems with HS the electron mean free path is small and therefore the alloy smearing of the Fermi surface has to be essential.

The alternative mechanism is proposed in the present work basing on the considerations of the closest packing of atoms for small atomic groups and geometric frustrations connected with them which may lead to the formation of HS with characteristic scale of order of few interatomic distances. The model proposed is rather rough and pretends to describe only some main features of the phenomenon. Nevertheless it stress, to our opinion, a peculiar role of the factor which is important for many real systems but was not taken into account in previous works.

Consider the precipitates of A15 phase in bcc host (e.g. of  $W_3Re$  phase in the solid solution  $W_{1-x}Re_x$  [11]) as an example of heterogeneous state of the type under consideration because A15 structure is the simplest and most well-known representative of FK phases [1]. It contains eight atoms per cell, two of them having icosahedral coordination and six of them being surrounded by polyhedra with 14 vertices [6]. The latter may be obtained from the regular icosahedron by the introducing of the edge disclination with the axis passing its center and the Frank vector  $-2\pi/5$ . Using such a procedure it was shown in Ref.6 that the net of SD for A15 structure consists from three mutually orthogonal sets of equidistant parallel disclinations with the period being equal to the lattice constant  $a$ . Other FK phases differs from A15 structure only by the geometry of SD net.

To solve the question about the stability of HS one needs to generalize the approach [6]. For this aim we use the basic relation between the curvature tensor  $R_{ijkl}$  and the disclination density tensor  $\theta_{ij}^{(c)}$  [14]

$$R_{ijkl} = -\epsilon_{ijp}\epsilon_{klq}\theta_{pq}^{(c)}, \quad (1)$$

where  $\epsilon_{ijp}$  is the unit antisymmetric tensor. In light of Eq. (1) the space curvature providing the ideal tetrahedral packing in the approach [1,6] is created by the introducing of the partial edge disclinations with Frank vector  $\Omega = 7^\circ 20'$  which compensate the deficiency of dihedral angles at the packing of five tetrahedra around the common edge [16]. To construct FK phases it is necessary to “decurve” the space by the introducing of SD with the average density  $\bar{\theta}_{ij}^{SD} = -\theta_{ij}^{(c)}$  where the line means the average over the volume containing large enough number of cells. Thus, in contrast with the approach of Ref.6 where SD were introduced in *curved* space we introduce *two* sets of disclinations in *Euclidean* space with the mean total density being equal to zero. At the same time local variation of the curvative of the lattice (i.e. the deviation of *local* disclination density from zero) is possible and connected with the elastic distortions of the bonds. The corresponding stresses are similar to that which have discussed in Ref.5 for glasses.

Apart from the energy of elastic distortions the electronic (“chemical”) contribution to the energy describing the tendency to the closest packing of atoms also exist. If in some place the density of SD differs from the mean density in the FK phase and therefore according to (1) the lattice appears to be locally curved the local values of the packing density will be higher or lower than in the FK phase.

In the framework of the approach considered the energy of the FK phase counted from the energy of the “host” phase with  $\theta = 0$  may be written as

$$E = \int d\mathbf{r} f[\theta_{ij}(\mathbf{r})] + E_{el}, \quad (2)$$

where  $f$  is the density of “chemical” energy depending on the degree of the atomic packing which is connected with the disclination density tensor  $\theta_{ij}$ ,  $E_{el}$  is the elastic energy. As usual [17] the latter may be represented in linear elasticity theory in the following form

$$E_{el} = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \eta^{\nu\rho}(\mathbf{r}) H_{\nu\rho\kappa\tau}(\mathbf{r} - \mathbf{r}') \eta^{\kappa\tau}(\mathbf{r}'), \quad (3)$$

where  $H_{\nu\rho\kappa\tau}$  is the Green tensor for internal stresses,  $\eta_{\nu\rho}$  is the incompatibility tensor de-

scribing the density of sources of internal stresses. According to [14] it is defined as

$$\eta^{\nu\rho} = -\frac{1}{2}(\epsilon_{\rho pq}\alpha_{\nu q,p} + \theta_{\nu\rho} + \epsilon_{\nu pq}\alpha_{\rho q,p} + \theta_{\rho\nu}), \quad (4)$$

where  $\alpha_{\nu\rho}$  is the disclination density tensor. Separating the singular part of the Green tensor we may represent the energy  $E_{el}$  as the sum  $E_{el} = E_{el}^{(0)} + E_{el}^{(1)}$  of the energy of distortions in the disclination cores  $E_{el}^{(0)}$  and the energy of elastic deformations outside the cores  $E_{el}^{(1)}$ .

When dislocations are absent one has  $\eta_{\nu\rho} = -1/2(\theta_{\nu\rho} + \theta_{\rho\nu})$ . For single disclination with the Frank vector  $(0,0,\Omega)$  the tensor  $\eta_{\nu\rho} = -\theta_{\nu\rho}$  has the only non zero component [14]

$$\eta^{33} = -\Omega\delta(\rho), \quad (5)$$

where  $\rho = (x, y)$ . In the case of the only set of edge disclinations considered here the tensor  $\theta_{ij}$  according to (5) may be characterized by the only scalar parameter  $\theta = Tr\theta_{ij}$  which equals to the mean value of the Frank vector in a given point. It is proportional to the scalar curvature  $R_{ijij}$  (see (1)). For the given geometry the energy of disclination cores (per unit length) may be represented as

$$\frac{E_{el}^{(0)}}{L} = e_0 \int d^2\rho \theta^2(\rho)$$

where  $e_0$  is the energy of the core of the disclination with unit Frank vector determining by the relation  $e_0\delta(\rho) = \frac{1}{2}H_{3333}(0)$ . Note that for the elastic continuum  $e_0 = 0$  and it is necessary to use the quasicontinuum model [17] to describe the core energy correctly.

It is a common practice in the material science to treat inhomogeneous state mainly as the multiphase state with the coexistence of regions with different crystal structures each of them may be stable in principle in the whole space. In this case the inhomogeneity may be described in terms of elastic distortions due to the conjugation of crystal lattices on the boundary of the precipitate and the host. To calculate the distortions the Eshelby model [15] is usually used, their energy appearing to be proportional to the volume of the precipitate. It is the consequence of the fact that in the Eshelby model the deformation  $\varepsilon_{ij}^{(0)}$  connected with the phase transition is constant inside the precipitate. Then, according to Eshelby,

the deformation  $\varepsilon_{ij}^{(0)}$  may be simulated by a system of disclination loops on the boundary of the precipitate. Since the energy of every loop is proportional to its radius  $R$  (equal to precipitate radius) and the number of loops is proportional to  $R^2$  their total energy turns out to be proportional to  $R^3$ . In our model the precipitate has the type of short-range order (e.g. icosahedral) which cannot correspond to long-range order for any bulk crystal phase. Therefore in contrast with the Eshelby model the deformation appears to be inhomogeneous not only outside the precipitate but also inside it. As the result it will be shown below that the elastic energy of the precipitate grows with the increase of  $R$  faster than  $R^3$  and therefore the stabilization of HS becomes possible.

The real form of the function  $f(\theta)$  in (2) is unknown. In accordance with our choice of the zero point for the energy we have for host phase ( $\theta = 0$ )  $f(0) = 0$  and the minimum of  $f(\theta)$  lies at the value  $\theta = \theta_0$  corresponding to the closest tetrahedral packing in the Riemannian space [2]. We suppose for the simplicity

$$f = \alpha(\theta - 2\theta_0)\theta, \quad (0 < \theta < \theta_0), \quad (6)$$

where the parameter  $\alpha > 0$  depends on the explicit form of the interatomic interactions. Generally speaking, the function  $f$  may contain also terms proportional to  $(\nabla\theta)^2$ , but in the framework of the variational approach used below (see (8)) they do not influence on the results.

To demonstrate the possibility of the formation of heterogeneous state we use the direct variational approach and construct explicitly the distribution  $\theta(r) \neq const$  leading to the lower value of the total energy than the homogeneous state. The problem may be solved in the simplest way for the cylindrical precipitate of the close packed phase. Let  $Oz$  be the axis and  $R$  the radius of the precipitate, the axis of all the disclinations are parallel to  $Oz$  and  $\theta = \theta(\rho)$  where  $\rho = \sqrt{x^2 + y^2}$ .

Since it is obvious that the discontinuities on the boundary between the host and precipitate are energetically unfavorable we restrict ourselves by the case of their coherent conjugation when the discontinuities are absent. In this case the disclinations cannot abrupt at

the boundary and should form loops with external segments in the host. In contrast with the homogeneous A15 phase the "polarized" distribution of disclinations is typical for our case namely the uniform distribution of positive partial disclinations inside the precipitate and the "cloud" of negative disclinations outside it. From topological considerations (the vanishing of the total Frank vector) one has

$$\int d^2\rho \theta(\rho) = 0 \quad (7)$$

To evaluate the minimum of the energy (2) we use the trial function

$$\theta(\rho) = \begin{cases} \theta_1, & \rho < R \\ \frac{-\theta_1 R^2}{2R\Delta + \Delta^2}, & R < \rho < R + \Delta \\ 0, & \rho > R + \Delta \end{cases} \quad (8)$$

answering the requirement (7) automatically. The value  $\Delta$  describes the thickness of the "cloud" and should be found from the solution of the variational problem. In the model under consideration the energy of elastic distortions concentrated in the disclination cores in the cloud would play the role of the surface energy. However, due to the condition (7) the total number of disclinations in the cloud is equal to that in the precipitate itself and is proportional to its volume (in 2D case  $\sim R^2$ ). Therefore in contrast with the Eshelby model it is impossible to separate explicitly the bulk and surface parts from the precipitate energy.

We use for  $H_{3333}(\rho - \rho') = H(\rho - \rho')$  the known expression [17]

$$H(r) = -\frac{2\mu}{1-\nu} \frac{\rho^2}{8\pi} \left[ 1 - \ln \frac{\rho}{R_c} \right] + C \quad (9)$$

corresponding to the continual approximation in the elastically isotropic model where  $\mu$  is the shear modulus,  $\nu$  is the Poisson ratio,  $R_c$  is the cutoff radius of order of the size of a crystal,  $C$  is the constant which does not contribute to the energy  $E_{el}^{(1)}$  for a given geometry (total Frank vector equals zero). To describe the energy of disclination cores  $E_{el}^{(0)}$  correctly one should use the quasicontinuum approximation [17]

$$C = -\frac{\mu}{2\pi(1-\nu)k_d^2} [1 + 2\gamma \ln k_d R_c]$$

where  $k_d$  is the Debye wave vector,  $\gamma$  is the parameter depending on the explicit form of phonon dispersion curves in the model.

Then the elastic energy (3) per unit length of the precipitate does not depend on the cutoff radius  $R_c$  and has the form

$$\frac{E_{el}^{(1)}}{L} = \theta_1^2 \frac{\mu a^4}{1-\nu} \tilde{\psi}(R, \Delta) \quad (10)$$

where

$$\begin{aligned} \tilde{\psi}(R, \Delta) = & \frac{R^4(\Delta + R)^2}{192a^4\Delta^2(\Delta + 2R)^2} \\ & \left[ \Delta(5\Delta^3 + 20\Delta^2R + 26\Delta R^2 + 12R^3) \right. \\ & \left. - 12R^2(\Delta + R)^2 \ln\left(\frac{\Delta + R}{R}\right) \right] \end{aligned}$$

The minimizing of the function  $\tilde{\psi}(R, \Delta)$  with respect to  $\Delta$  gives the dependence of the cloud thickness  $\Delta = \Delta(R)$ . As a result the total energy may be represented in the following form

$$\frac{E}{L} = \pi R^2 \alpha p (\theta_1 - 2\tilde{\theta}_0) \theta_1 + \theta_1^2 \frac{\mu a^4}{1-\nu} \psi(R) \quad (11)$$

where  $\psi(R) = \tilde{\psi}(R, \Delta(R))$ ,  $\tilde{\theta}_0 = \theta_0/p$ ,  $p = 1 + 2e_0/\alpha$ . The minimum of energy (11) corresponds to the disclination density

$$\theta_1 = \frac{\tilde{\theta}_0}{1 + \psi(R)/\kappa R^2}, \quad (12)$$

where the precipitate radius  $R$  is found from the equation

$$R \frac{d\psi(R)}{dR} = 2(2\psi(R) + \kappa R^2) \quad (13)$$

Here

$$\kappa = \frac{\delta f(1-\nu)\pi p}{\mu a^4 \theta_0^2} \quad (14)$$

and the value  $\delta f = \alpha \theta_0^2$  describes the chemical energy gain (per unit volume) at the transition to the ideal tetrahedral packing.

As it follows from Eq. (13) the precipitate radius  $R$  depends on the parameter  $\kappa$  characterizing the ratio of the chemical contribution to the elastic one. According to (14) its

value varies from 0.1 to 1 at  $\delta f \approx 0.01 - 0.1$  eV per atom. Direct calculations show that in all these limits of the variation of  $\kappa$  the function  $\psi(R)$  is almost constant at  $R < 2a$  and increases sharply at  $R > 3a$ . On that ground, the equilibrium value of  $R$  grows slowly with  $\kappa$  increase (see Fig.1). At  $\kappa < 0.1$  the continual approach under consideration does not hold because  $R < a$ . In this range of values of  $\kappa$  the disclination density  $\theta_1$  determined by Eq. (12) is less than the minimal possible value corresponding one disclination with Frank vector  $7^\circ 20'$  per precipitate.

The spatial distribution of the dilatation obtained by numerical integration is shown in Fig.2. One may see that the internal part of the precipitate is expanded and the dilatation  $\varepsilon_{ll}$  vanishes sharply at the boundary. The mean value in the precipitate  $\langle \varepsilon_{ll} \rangle$  increases approximately linear with the precipitate radius. This demonstrates the qualitative difference between the model under consideration and the Eshelby model. Since the average deformation increases with  $R$  increasing the elastic energy will grow faster than  $R^2$  in 2D case ( or than  $R^3$  for spherical precipitate).

Putting the equilibrium values of  $\theta_1, R$  in Eq.(11) one obtains the expressions for the energy change at the formation of the precipitate

$$\frac{E}{L} = -\delta f \pi R^2 \frac{\theta_1}{\theta_0} = -\frac{\theta_0 \theta_1^2}{\theta_0 - \theta_1} \frac{\mu a^4 \psi(R)}{1 - \nu} < 0 \quad (15)$$

Thus in the model under consideration the precipitates are stable and the heterogeneous state has the lower energy than the bcc lattice. Accordingly to the dependence  $\theta_1$  on  $R$  its value (12) , generally speaking, is not coincide with one of the values corresponding homogeneous FK phases.

Thus we show that for certain ratio between "chemical" and elastic properties of the media ( $\kappa \geq 0.1$ ) the heterogeneous state may be energetically favorable owing to the crystallogometrical factors (tendency to the closest local packing). It is worthwhile to stress again the most important features of this state in the framework of the model under consideration (i) sizes of the precipitates are of order of few lattice constants (ii) the structure of precipitates is distorted in comparison with the structures of FK phases in an infinite

crystal (iii) precipitates are surrounded by the cloud of the distorted host lattice with the thickness of order of the sizes of the precipitates. The existence of this cloud has an obvious sense: since it is impossible to fill the whole space by the regular tetrahedra an attempt to realize such filling locally in some part of the space results inevitably to the appearance of voids at the boundary. The introducing of the external segments of disclination loops lead to the elimination of these voids and coherent conjugation of the precipitate with the host surrounded.

In the specific case when the host phase is bcc a sharp increase of the solubility of light interstitial impurities is one of the characteristic features of the mechanism considered of the formation of HS. It is connected with the presence of large tetrahedral voids in close packed structures and their absence in bcc lattice. This feature together with the change of the type of short-range order and the appearance of elastic distortions can help to identify this kind of HS experimentally.

The results obtained here may explain some important features of the so called "rhenium effect" (the improvement of the ductility of W and Mo at the doping by Re). According to Ref. 11 the increase of the solubility of interstitial impurities connected with the appearance of the precipitates of the FK phases in particular  $W_3Re$  is the key feature in this phenomenon. The results presented here allows us, on the one hand, to understand the causes of the appearance of the precipitates and, on the other hand, to point out the specific mechanism of their influence on the solubility of interstitial impurities. Indeed, considerable dilatation in the cloud surrounded the precipitate may lead to the essential energy gain at the transfer of the interstitial atom from the host to the shell. It may prevent the appearance of the carbide precipitates or impurity segregation at the intergrain boundaries.

Note in the conclusion that the transition from the two-dimensional case considered here to the three-dimensional one is not trivial since to "dress" the spherical precipitate by the cloud of compensated defects we cannot restrict ourselves by the disclinations only and it is necessary to introduce the density of disclination loops as an additional variable. However the results presented here seem to be sufficient to demonstrate the instability of

the homogeneous state under some conditions.

To resume it is worthwhile to note that the present work show the interconnection of some specific facts known in the material science with non-trivial properties of three-dimensional space and therefore demonstrate the general physical meaning of these facts.

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## FIGURES

FIG. 1. The dependence of the equilibrium values of precipitate radius  $R$ , disclination density  $\theta_1$  (in units of  $\tilde{\theta}_0$ ) and the value of  $\psi$  in Eq.(11) on the  $\kappa$  parameter (14).

FIG. 2. The distribution of the dilatation  $\varepsilon_{kk}$  in the precipitate (solid line) on the polar coordinate  $r$  ( $R=4$ ,  $\Delta = 1$ ), and the dependence of *average* dilatation  $\langle \varepsilon_{kk} \rangle$  on the precipitate radius  $R$  (dashed line) in the units  $\theta_1(1 - 2\nu)/(2\pi(1 - \nu))$ .



